Science of the Total Environment 653 (2019) 496–503

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Secondary organic aerosol of $PM_{2.5}$ in a mountainous forest area in southeastern China: Molecular compositions and tracers implication

Zhenyu Hong [a,b,c], Han Zhang [a,b], Yanru Zhang [a,b,c], Lingling Xu [a,b], Taotao Liu [a,b,c], Hang Xiao [a,b], Youwei Hong [a,b,*], Jinsheng Chen [a,b,*], Mengren Li [a,b], Junjun Deng [a,b], Xin Wu [a,b,c], Baoye Hu [a,b,c], Xiaoqiu Chen [d]

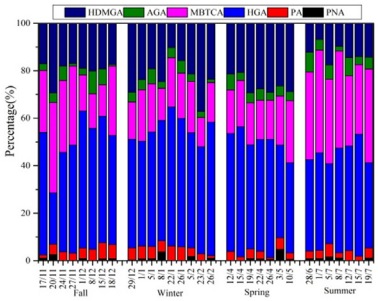
[a] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[b] Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[c] University of Chinese Academy of Sciences, Beijing 100086, China
[d] Environmental Monitoring Center of Fujian, Fuzhou 350003, China

## HIGHLIGHTS

- $PM_{2.5}$-bound SOA tracers in a mountainous area of southeastern China were firstly investigated.
- Analysis of $\alpha$/$\beta$-pinene tracers indicated that SOA were highly oxidized on Mt. Wuyi.
- Biomass burning events affected by local and regional sources were identified.
- SOC in $PM_{2.5}$ were estimated using the tracer-based method.

## GRAPHICAL ABSTRACT

Mountainous forest area




Aerosol aging

## ARTICLE INFO

*Article history:*
Received 21 August 2018
Received in revised form 27 October 2018
Accepted 27 October 2018
Available online 30 October 2018

Editor: Jianmin Chen

*Keywords:*
Secondary organic aerosol (SOA) tracers
$PM_{2.5}$
Secondary organic carbon (SOC)
Mountainous forest area
Biomass burning

## ABSTRACT

Secondary organic aerosol (SOA) plays an important role in global climate change and air quality. $PM_{2.5}$ (particles with aerodynamic diameters ≤2.5 μm) samples were collected at a mountainous forest site (Mt. Wuyi) in southeastern China between November 2015 and July 2016. Fourteen $PM_{2.5}$-bound SOA tracers, including isoprene, $\alpha$/$\beta$-pinene, $\beta$-caryophyllene, and toluene, were measured using the gas-chromatography–mass-spectrometry method. The total concentrations of the isoprene, $\alpha$/$\beta$-pinene, $\beta$-caryophyllene, and toluene SOA tracers were 45.28 ± 65.52, 30.66 ± 24.44, 5.99 ± 7.25, and 0.62 ± 0.72 ng $m^{-3}$, respectively. The isoprene SOA tracers exhibited the highest concentration (145.97 ± 53.78 ng $m^{-3}$) and accounted for 76 ± 9% of the total concentration of SOA tracers in summer. In fall-winter, the mass fraction of 2-methylglyceric acid was significantly enhanced because of the lower temperature and higher $NO_x$ level. As later-generation products of $\alpha$/$\beta$-pinene tracers, high proportions of 3-hydroxyglutaric acid and 3-methyl-1,2,3 butanetricarboxylic acid were observed on Mt. Wuyi, suggesting that the aerosols were highly oxidized. Biomass burning events affected by local and regional sources were identified by analyzing typical SOA tracers. Significant positive correlation ($R^2$ = 0.74) was found between the $\beta$-caryophyllene tracer and levoglucosan. The average concentration of secondary organic carbon (SOC) as estimated from SOA tracers was 1.46 μgC $m^{-3}$. The isoprene SOC accounted for 70% of the total SOC in summer, whereas the $\beta$-caryophyllene SOC was the predominant component in winter. Meanwhile, the

* Corresponding authors at: Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
*E-mail addresses:* ywhong@iue.ac.cn (Y. Hong), jschen@iue.ac.cn (J. Chen).

https://doi.org/10.1016/j.scitotenv.2018.10.370
0048-9697/© 2018 Elsevier B.V. All rights reserved.

estimated toluene SOC accounted for 11.6% of the total SOC during the study period. The study helps understanding the characteristics and the formation of SOA in a mountainous forest area of southeastern China.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Secondary organic aerosol (SOA) is the major component of atmospheric fine particulate ($PM_{2.5}$) and plays an important role in climate change, air quality, cloud condensation, and human health (Jimenez et al., 2009). SOA can be formed by both homogenous and heterogeneous reactions of volatile organic compounds (VOCs) emitted from biogenic and anthropogenic sources (Jang et al., 2002; Claeys et al., 2004). On a global scale, emissions of biogenic VOCs (BVOCs), which comprise mainly isoprene, monoterpenes (such as $\alpha/\beta$-pinene), and sesquiterpenes (such as $\beta$-caryophyllene), are estimated to be one order of magnitude higher than those of anthropogenic VOCs (such as toluene) (Guenther et al., 2006). Therefore, most global SOA is believed to be transformed from BVOCs. However, the processes of SOA formation and transformation remain uncertain (Shrivastava et al., 2017).

SOA tracers can provide some insights into the sources and processes that influence SOA formation. Arising mainly from terrestrial vegetation and partly from the oceans, isoprene is the most abundant species among the various BVOCs (Guenther et al., 2006). 2-methyltetrols (MTLs; the sum of 2-methylthreitol (MTL1) and 2-methylerythritol (MTL2)) and C5-alkene triols were the unique oxidation products of isoprene, while MTLs were detected in Amazonian aerosols and C5-alkene triols were important under conditions of low $NO_x$ (Surratt et al., 2006). Monoterpenes and sesquiterpenes were two other main BVOCs that contribute significantly to SOA (Griffin et al., 1999; Duhl et al., 2008). As the most abundant species of monoterpenes, $\alpha/\beta$-pinene can be formed by pinic acid (PA) and pinonic acid (PNA) or by photooxidation of 3-hydroxyglutaric acid (HGA) and 3-methyl-1,2,3 butanetricarboxylic acid (MBTCA) (Eddingsaas et al., 2012). $\beta$-Caryophyllene is one of the most abundant species of sesquiterpenes and can be identified by the specific tracer $\beta$-caryophyllinic acid. Identifying aromatic SOA tracers (2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)) made it possible to evaluate the contribution of SOA from anthropogenic sources, especially in urban areas (Offenberg et al., 2007).

In recent years, the formation of biogenic SOA (BSOA) has been studied in chamber experiments (e.g., D'Ambro et al., 2017; Faust et al., 2017; Palm et al., 2017), ambient aerosols from urban areas (e.g., Hu et al., 2008; Stone et al., 2010; Feng et al., 2013; Ding et al., 2016; Fu et al., 2016), and the ocean (Fu et al., 2009, 2013; Ding et al., 2013; Hu et al., 2013). However, there have been relatively few studies of BSOA in mountainous forest areas (e.g., Fu et al., 2010; Stone et al., 2012; Li et al., 2013). Mountainous forest areas offer a unique environment in which to study SOA formation and sources (Fu et al., 2014a). The active airflow at a mountain top is more susceptible to long-range transportation of $PM_{2.5}$ and can reflect the characteristics of the atmosphere. Studying BSOA tracers in mountainous areas could improve our understanding of (i) the chemical properties of organic aerosols in the atmosphere and (ii) the transmission of pollution.

In the present study, the molecular compositions and seasonal patterns of SOA tracers on Mt. Wuyi (altitude: 1139 m) were investigated for the first time, this being a mountainous forest area in southeastern China. Typical SOA tracers were chosen as the indicators of $NO_x$ level and aging process of SOA. The temporal variations of SOA tracers during a local and a regional biomass burning events were investigated. The concentration of biogenic secondary organic carbon (SOC) was also estimated using the tracer-based method.

## 2. Materials and methods

### 2.1. Sampling site

The sampling site (27.35°N, 117.43°E) is located in Mt. Wuyi Nature Reserve in the northern part of Fujian Province, south east China, at an altitude of 1139 m. Samplers were installed on the rooftop of the building of the Mt. Wuyi national atmospheric background monitoring station, with a height of 15 m above ground. Mt. Wuyi is the best representation of an intact and ecologically diverse forest in the subtropical region of China. The annual precipitation is in excess of 2000 mm and the annual relative humidity is around 85%. The area surrounding the site is open and the airflow is active. Because the site contains no significant anthropogenic sources of air pollution, it can objectively reflect the influences of biogenic emission sources and regional transportation of pollutants on air quality in southeastern China (Fig. 1).

### 2.2. Sample collection

The sampling campaigns were conducted on Mt. Wuyi in November 17, 2015–February 26, 2016 (fall-winter), April 12–May 10 (spring) and June 28–July 19 (summer) of 2016. Seventy-two-hour $PM_{2.5}$ samples were collected continuously on preheated (500 °C, 4 h) quartz filters (8 × 10 in., Whatman) using a high-volume sampler (TH1000H, Wuhan Tianhong, China) at a flow rate of 1.05 $m^3$ $min^{-1}$. The average temperature and relative humidity (RH) were 9.0 °C and 79.5% in fall-winter, 17.2 and 84.9% in spring, 24.1 °C and 75.7% in summer, respectively (Table S1). Thirty-three samples and four field blanks were collected during the study period. The sampled filters were covered with aluminum foil and stored at −20 °C until analysis.

### 2.3. Chemical analysis

Aliquots of the filters (ca. 5 $cm^2$) were cut and then extracted for three times with 10 mL dichloromethane/methanol (2:1, v/v) under ultrasonication for 10 min. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated by a rotary evaporator, and blown dry by a flow of high-purity nitrogen. The extracts were then derivatized with 50 μL of *N,O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h to convert COOH groups to esters and OH groups to trimethylsilyl ethers. The analytical procedure of SOA tracers is described elsewhere (Fu et al., 2010).

The derivatized extracts were analyzed in a gas-chromatography-mass-spectrometer (GC–MS) detector (Agilent 7890A/5975C, Agilent Technologies, Inc., USA) with a DB-5 MS fused silica capillary column (i.d. 30 × 0.25 mm, 0.5 μm film thickness). Prior to the analysis, $C_{13}$ *n*-alkane was spiked into the extracts as an internal standard. One microliter of the sample was injected in splitless mode at 280 °C and high-purity helium (99.999%) was used as the carrier gas at a stable flow of 1.0 mL $min^{-1}$. The GC temperature was initiated at 50 °C (held for 2 min) then increased to 120 °C at 15 °C $min^{-1}$ and then to 300 °C at 5 °C $min^{-1}$, and finally kept at 300 °C for 16 min. The MS was operated in electron ionization (EI) mode at 70 eV and the MS scanned from *m/z* 50 to *m/z* 650.

Levoglucosan, malic acid, HGA, PNA, and PA were quantified using authentic standards. Because of the lack of commercial standards, $\alpha/\beta$-pinene SOA tracers including MBTCA, 3-acetylglutaric acid (AGA), and 3-hydro-4,4-dimethyglutaric acid (HDMGA) were determined

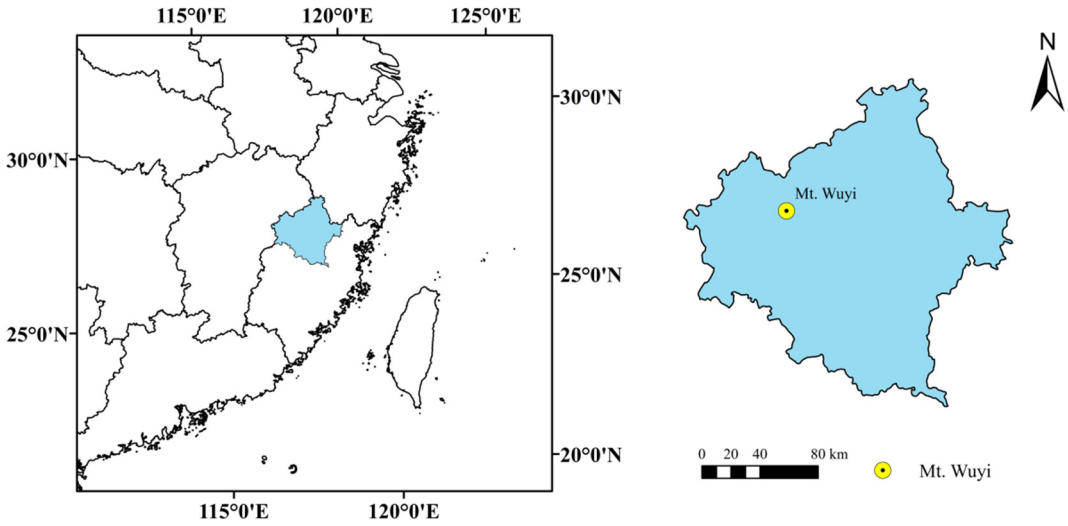



**Fig. 1.** Location of sampling site on Mt. Wuyi in southeastern China.

using malic acid as a standard. β-Caryophyllinic acid was estimated using the response factor of PA. Isoprene SOA tracers including MGA, C5-alkene triols (*cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene), and MTLs were quantified using erythritol as a standard (Fu et al., 2010; Haddad et al., 2011).

The EC and OC of $PM_{2.5}$ samples were determined on a 1.5 $cm^2$ filter by using a carbon analyzer (Sunset Model-4, USA) with the thermal-optical transmittance (TOT) method, following the National Institute for Occupational Safety and Health (NIOSH) protocol (Birch and Cary, 1996).

### 2.4. Quality control and quality assurance

Field blanks were collected during the sampling periods by using filters on the sampler without pumping any air for 72 h. After being extracted and measured in the same way as the field samples, none of the target compounds were found in the field blanks. The recovery rates of erythritol, HGA, PNA, PA, and malic acid were 71 ± 6%, 85 ± 10%, 62 ± 11%, 65 ± 7%, and 85 ± 8%, respectively. In duplicate samples ($n = 5$), the target compounds all differed by <13%. The reported concentrations of SOA tracers were not corrected for recovery.

### 2.5. Data analysis

#### 2.5.1. Statistical analysis

The relationships among SOA tracers were investigated by Pearson correlation analysis. Seasonal variations in the concentration and the proportion of individual SOA tracers were examined by one-way ANOVA (Analysis of Variance), and the variations were all significant at the level of 0.05 in this study.

#### 2.5.2. Estimation of SOC

The tracer-based method was used to estimate the fractions of SOC formed through the oxidation of isoprene, α/β-pinene, β-caryophyllene, or toluene. Kleindienst et al. (2007) derived the mass fraction of tracer compounds in SOA generated from individual precursors by using smog-chamber experimental data for different hydrocarbon/$NO_x$ mixtures; this is defined as $[SOC] = \sum_i [tr_i] / f_{SOC}$, where [SOC] is the mass concentration of SOC (μg C $m^{-3}$) and $\sum_i [tr_i]$ is the sum of the concentrations of the tracers for a certain precursor (μg $m^{-3}$). The carbon mass fractions ($f_{SOC}$) of the tracer compounds in the laboratory-generated SOC from isoprene, α/β-pinene, β-caryophyllene, and toluene were 0.155 ± 0.111, 0.231 ± 0.111, 0.023 ± 0.0046, and 0.0079 ± 0.0026, respectively, which were proposed by Kleindienst et al. (2007) based on the smog-chamber experimental data. Assumption that the smog-chamber $f_{SOC}$ values are the same as those in the ambient air, SOC from different precursors was estimated by SOA tracers in this study.

## 3. Results and discussion

### 3.1. Overall concentrations of SOA tracers

The concentrations of organic carbon (OC), element carbon (EC), and SOA tracers are listed in Table 1. The total isoprene SOA tracers (45.28 ± 65.52 ng $m^{-3}$) were more abundant than those of α/β-pinene (30.66 ± 24.44 ng $m^{-3}$), β-caryophyllene (5.99 ± 7.25 ng $m^{-3}$), and toluene (0.62 ± 0.72 ng $m^{-3}$). The temporal variations of isoprene, α/β-pinene, β-caryophyllene, and toluene SOA tracers were plotted in Fig. 2. The concentrations of total SOA tracers were much higher in summer and spring than those in fall-winter. The isoprene SOA tracers exhibited particularly high concentrations in summer, accounting for 76 ± 9% of all SOA tracers. In mountainous areas, biogenic emissions are the major sources of SOA, especially in summer when all the plants are growing vigorously (Fu et al., 2010). Higher temperatures and stronger solar radiation increase isoprene emissions and their photoreactions. Higher temperatures also enhance the heterogeneous reactions of isoprene-derived epoxides on particles, and the reactions play important roles in forming isoprene SOA (Paulot and Wennberg, 2009; Lin et al., 2013). As described above, isoprene emission depends heavily on temperature. Because of the relatively low temperatures in fall-winter (average 9.0 °C, Table S1), the amount of isoprene emitted by plants was much lower in those seasons (decreasing by 90% from summer to fall-winter; Fig. 2). In addition, α/β-pinene SOA tracers were more abundant than isoprene SOA tracers in every season except summer. As a β-caryophyllene (a sesquiterpene) oxidation product (Jaoui et al., 2007), β-caryophyllinic acid exhibited relative high concentrations (5.99 ± 7.25 ng $m^{-3}$) in winter, which was probably due to biomass burning.

In Table 2, the concentrations of isoprene, α/β-pinene, β-caryophyllene, and toluene products on Mt. Wuyi were compared with those in other regions around the world. The related BSOA (isoprene, α/β-pinene and β-caryophyllene) tracers were presented in particularly high concentrations on Mt. Wuyi comparing to other areas except for Mt. Tai. The summer concentrations of BSOA tracers on Mt. Wuyi were similar to those on Mt. Tai except for β-caryophyllinic acid. Mt. Tai is located in Central East China on the transport path of the

**Table 1**
Concentrations (ng $m^{-3}$) of secondary organic aerosol (SOA) tracers and their percentages in organic carbon (OC) during the study period on Mt. Wuyi.

| Major components | Average | Range | %C in OC |
|---|---|---|---|
| OC (μgC $m^{-3}$) | 2.27 ± 1.46 | 0.4–5.38 | |
| EC (μgC $m^{-3}$) | 0.31 ± 0.28 | 0.06–0.58 | |
| Isoprene SOA tracer | | | |
| 2-Methylglyceric acid (MGA) | 1.38 ± 0.72 | 0.05–3.36 | 0.08 |
| 2-Methylthreitol (MTL1) | 8.07 ± 11.06 | 0.05–43.12 | 0.45 |
| 2-Methylerythritol (MTL2) | 24.48 ± 39.06 | 0.39–148.1 | 1.42 |
| 2-Methyltetrols (MTL) | 32.55 ± 48.84 | 0.05–148.1 | 1.86 |
| *cis*-2-Methyl-1,3,4-trihydroxy-1-butene | 3.5 ± 5.64 | nd[a]–20.51 | 0.22 |
| 3-Methyl-2,3,4-trihydroxy-1-butene | 1.49 ± 2.37 | nd–7.52 | 0.10 |
| *trans*-2-Methyl-1,3,4-trihydroxy-1-butene | 6.37 ± 10.12 | 0.1–43.15 | 0.37 |
| C5-alkene triols[b] | 11.35 ± 18.13 | 0.08–59.23 | 0.67 |
| Sum of isoprene SOA tracer | 45.28 ± 65.52 | 1.13–221.5 | 2.61 |
| α/β-Pinene SOA tracer | | | |
| 3-Hydroxyglutaric acid (HGA) | 13.32 ± 9.36 | 2.34–43.93 | 0.51 |
| Pinic acid (PA) | 1.22 ± 1.25 | 0.22–5.49 | 0.07 |
| Pinonic acid (PNA) | 0.41 ± 0.95 | nd–5.37 | 0.03 |
| 3-Methyl-1,2,3 butanetricarboxylic acid (MBTCA) | 7.8 ± 6.08 | 0.43–23.24 | 0.41 |
| 3-Acetylglutaric acid (AGA) | 1.37 ± 1.18 | 0.13–20.82 | 0.22 |
| 3-Hydroxy-4,4-dimethylglutaric acid (HDMGA) | 6.55 ± 6.24 | 0.6–29.66 | 0.28 |
| Sum of α/β-pinene SOA tracer | 30.66 ± 24.44 | 0.79–112.51 | 1.42 |
| Toluene SOA tracer | | | |
| 2,3-Dihydroxy-4-oxopentanoic acid (DHOPA) | 0.62 ± 0.72 | nd–2.92 | 0.04 |
| β-Caryophyllene SOA tracer | | | |
| β-Caryophyllinic acid | 5.99 ± 7.25 | nd–35.21 | 0.26 |

[a] "nd" means not detected.
[b] The sum of *cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, and *trans*-2-methyl-1,3,4-trihydroxy-1-butene.

Asian continental outflow. Previous studies had indicated that the atmosphere on Mt. Tai is influenced significantly by biomass burning on the North China Plain during harvest time, which contributes large amounts of β-caryophyllinic acid. By contrast, the concentrations of isoprene SOA tracers on Mt. Wuyi were much higher than those on Mt. Changbai (Li et al., 2013). As an aromatic product, DHOPA is a typical oxidation product of toluene (aromatic hydrocarbons). The concentration of DHOPA on Mt. Wuyi (0.62 ng $m^{-3}$) was close to the value (0.4 ng $m^{-3}$) reported for the Tibetan Plateau but lower than those reported for different regions in China (average 2.9 ng $m^{-3}$; Ding et al., 2014) and a mountainous site in Hong Kong (average 2.1 ng $m^{-3}$; Lyu et al., 2017).

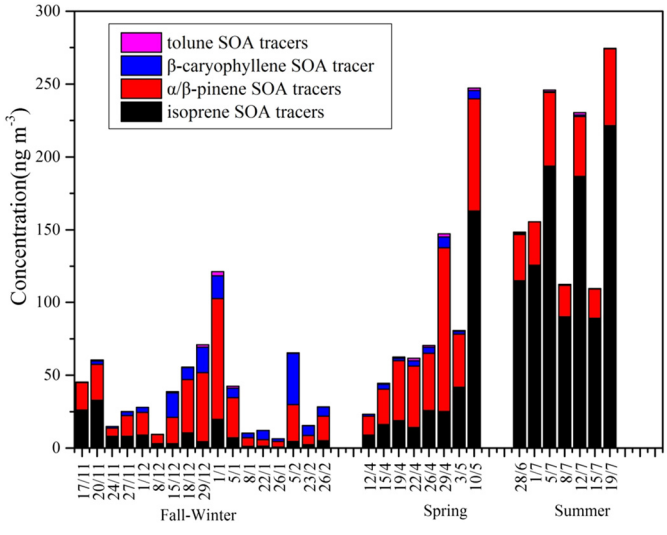



**Fig. 2.** Temporal variations of isoprene, α/β-pinene, β-caryophyllene, and toluene SOA tracers on Mt. Wuyi during the sampling period.

### 3.2. SOA tracers as indicators of atmospheric process

#### 3.2.1. Isoprene SOA tracers as indicator of $NO_x$ level

Six compounds were determined as oxidation products of isoprene, namely MGA, two types of MTL, and three types of C5-alkene triol (Table 1). The averaged MTL concentration (32.55 ± 48.84 ng $m^{-3}$) was higher than those of C5-alkene triols (11.35 ± 18.13 ng $m^{-3}$) and MGA (1.38 ± 0.72 ng $m^{-3}$) during the study period.

Isoprene epoxydiols (IEPOX) are important SOA intermediates under low-$NO_x$ conditions, forming initially in the gas phase and subsequently being partitioned into the aerosol aqueous phase (Paulot and Wennberg, 2009; Surratt and Finlayson-Pitts, 2010). IEPOX further converts to MTLs and C5-alkene triols through an acid-catalyzed ring opening of this epoxydiol and a subsequent nucleophilic addition (Li et al., 2013). In the present study, a positive correlation was found between MTLs and C5-alkene triols ($R^2 = 0.75$, $p < 0.01$; Fig. S1). Fig. 3 shows the percentages of individual isoprene SOA tracers on Mt. Wuyi. The results indicated that isoprene SOA tracers presented significantly temporal and seasonal variation. In summer, the percentages of MTLs and C5-alkene triols increased significantly to 90%, reflecting a low-$NO_x$ environment. By contrast, the percentages of MGA in fall-winter were significantly higher than those in spring and summer (Fig. 3). High $NO_x$ concentrations in fall-winter (average 3.2 and 4.3 μg $m^{-3}$, respectively; Table S1) were observed at the sampling site and likely contributed to the relatively high proportion of MGA. This is consistent with the fact that MGA is an oxidation product of isoprene produced under high-$NO_x$ conditions (Surratt and Finlayson-Pitts, 2010).

The ratio of MTLs to MGA exhibited the highest value in summer (77.2 ± 27.77), followed by spring (10.06 ± 15.74), fall-winter (4.61 ± 4.30) (Fig. 4a). High temperature (24.1 °C; Table S1), enhanced vertical convection, and low concentrations of $NO_x$ (2.1 μg $m^{-3}$; Table S1) in summer favored the formation of MTLs, contributing to the highest MTLs/MGA ratio. However, in fall-winter, the isoprene emission decreased significantly because of the relative low temperatures. Meanwhile, high concentrations of $NO_x$ favors the formation of MGA (Zhang et al., 2011), which is accounted for the reason why the MTLs/MGA ratio exhibited its lowest value in fall-winter. In the present study, the values of the MTLs/MGA ratio were higher than those on the Tibetan Plateau (>10 in summer and ~1.25 in winter; Shen et al., 2015) and aircraft (10 in summer and 2.8 in spring; Fu et al., 2014a, 2014b). Furthermore, the values of the MTLs/MGA ratio were one to two orders of magnitude higher than those in different regions of China (Ding et al., 2014, 2017) and the urban regions of the United States (Lewandowski et al., 2013).

#### 3.2.2. α/β-Pinene SOA tracers as indicator of aerosol aging

α/β-pinene is the most naturally occurring monoterpene, and monoterpenes contribute roughly 35% of BVOC global emissions (Griffin et al., 1999). In the present study, the photo-oxidation products of α/β-pinene including PNA, PA, AGA, HDMGA, MBTCA, and HGA were identified, and their average concentrations were 0.41 ± 0.95, 1.22 ± 1.25, 1.37 ± 1.18, 6.55 ± 6.24, 7.80 ± 6.08, and 13.32 ± 9.36 ng $m^{-3}$, respectively (Table 1).

Table 3 shows the concentrations of individual α/β-pinene tracers on Mt. Wuyi. The results indicated that HGA was the dominant species, accounting for 45.7 ± 7.7% of all the α/β-pinene tracers, while MBTCA and HDMGA accounted for 24.7 ± 9.4% and 20.2 ± 6.9% of the total α/β-pinene tracers, respectively. Previous studies had also found HGA to be the dominant α/β-pinene tracer (Kleindienst et al., 2007; Kourtchev et al., 2008; Lewandowski et al., 2008; Ding et al., 2011). Lyu et al. (2017) suggested that MBTCA and HGA were the dominant components of all measured α/β-pinene SOA tracers in $PM_{2.5}$ at a mountain site in Hong Kong. PA and PNA are generated by the oxidation of α/

**Table 2**
Concentrations (ng $m^{-3}$) of SOA tracers on Mt. Wuyi and in other regions of the world.

| Sampling site | Sampling type | Sampling period | Isoprene[a] products | α/β-Pinene products | β-Caryophyllene products | Aromatics products | Reference |
|---|---|---|---|---|---|---|---|
| Mt. Wuyi, China | $PM_{2.5}$ | Four seasons | 45.28 | 30.66 | 5.99 | 0.62 | This study |
| Mt. Wuyi, China | $PM_{2.5}$ | Summer | 145.97 | 31.32 | 4.73 | 0.40 | This study |
| Mt. Tai, China | TSP | Summer | 171 | 30 | 12 | NA[b] | Fu et al. (2010) |
| Mt. Hua, China | $PM_{10}$ | Summer | 13 | 6.6 | 2.2 | NA | Li et al. (2013) |
| Changbai, China | $PM_{2.5}$ | Summer | 53 | 31 | NA | NA | Wang et al. (2008) |
| Mt. Tai Mo Shan | $PM_{2.5}$ | Fall | 54.7 | 26.3 | 1.1 | 2.1 | Lyu et al. (2017) |
| Himalayas | $PM_{2.5}$ | Summer | 30.7 | 13.2 | 1.6 | NA | Stone et al. (2012) |
| Tibetan Plateau | Size-segregated particle | Four seasons | 26.6 | 0.97 | 0.09 | 0.25 | Shen et al. (2015) |
| Mt. Fuji | TSP | Summer | 69 | 39 | 0.36–1.6 | NA | Fu et al. (2014a) |
| Alert, Canada | $PM_{2.5}$ | Winter-summer | 0.3 | 1.6 | 0.12 | NA | Fu et al. (2009) |
| Arctic Ocean | $PM_{2.5}$ | Summer | 4 | 4.8 | 0.017 | NA | Fu et al. (2013) |
| Antarctic to Arctic | $PM_{2.5}$ | Summer | 8.5 | 3 | NA | NA | Hu et al. (2013) |
| North Pacific and Arctic | $PM_{2.5}$ | Summer | 0.62 | 0.06 | 0.0002 | nd[c] | Ding et al. (2013) |
| Hong Kong, China | $PM_{2.5}$ | Summer | 30 | 198 | 13 | NA | Hu et al. (2008) |
| Shanghai, China | $PM_{2.5}$ | Four seasons | 16.5 | 4.65 | 0.7 | NA | Feng et al. (2013) |
| Troposphere over Central China | $PM_{2.5}$ | Summer | 39 | 16 | 1.2 | NA | Fu et al. (2014b) |
| 14 sites, China | $PM_{2.5}$ | Summer | 123 | 10.5 | 5.07 | 2.9 | Ding et al. (2014) |

[a] Compositions are different in different studies.
[b] "NA" means not available.
[c] "nd" means not detected.

β-pinene via reactions with $O_3$ and OH radicals, and might be further transformed into MBTCA (Szmigielski et al., 2007; Hu et al., 2008). The ratio of (i) MBTCA to (ii) PA plus PNA (M/P) could be used to evaluate the aging degree of α/β-pinene SOA (Ding et al., 2014). A lower M/P ratio indicates less transformation of PA and PNA and thus reflects fresher α/β-pinene SOA, whereas a higher M/P ratio suggests older α/β-pinene SOA. According to chamber experiments, the values of M/P were 0.31–0.66 in the fresh products of α/β-pinene SOA (Offenberg et al., 2007). In the present study, M/P ranged from 1.75 to 15.64 with an average of 6.9 (Fig. 4b), suggesting that the aerosols on Mt. Wuyi were highly oxidized. The value of M/P in summer (9.55) was obviously higher than that in fall-winter (4.78). The higher temperatures and stronger radiation in summer might promote the SOA to become highly oxidized, thereby leading to more transformation of PA and PNA to MBTCA (Li et al., 2013). Previous studies in Okinawa presented similar findings (0.78 in November–April and 3.16 in May–October, Zhu et al., 2016).

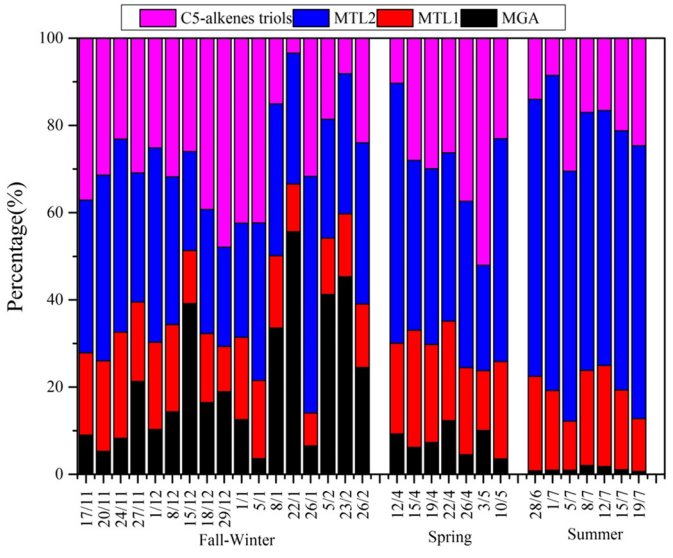



**Fig. 3.** Percentages of C5-alkenes triols, 2-methylglyceric acid (MGA), 2-methylthreitol (MTL1), and 2-methylerythritol (MTL2) in isoprene SOA tracer on Mt. Wuyi during the sampling period.

Previous studies have pointed out that HGA/MBTCA could be used to distinguish different monoterpenes, such as α-pinene SOA with higher yields of MBTCA and β-pinene with HGA (Jaoui et al., 2005; Ding et al., 2014). A study at 15 sites in the U.S. indicated that α-pinene was the major precursor for monoterpenes in the southeastern U.S. because of the lowest ratio of HGA/MBTCA there (~1.0, Lewandowski et al., 2013). The ratio of HGA/MBTCA ranged from 0.57 to 4.00 with an average of 2.2 on Mt. Wuyi (Fig. 4c), which was comparable to the values for 14 sites in China (0.75–5.07, Ding et al., 2014). The average ratio of HGA/MBTCA was lowest in summer (1.17), suggesting that α-pinene contributed more monoterpene SOA in summer than in other seasons on Mt. Wuyi.

### 3.3. Influence of biomass burning on SOA tracers

Biomass burning is an important source of atmospheric particles on a regional to global scale, and those particles have a significant impact on climate change (Mochida et al., 2010). Levoglucosan is a key tracer for biomass burning (Simoneit, 2002). The temporal variations of typical SOA tracers on Mt. Wuyi during the study period are shown in Fig. 5. The concentrations of levoglucosan in winter (from December 7 to February 26) were significantly higher than those in the other seasons, indicating the important influence of biomass burning on aerosols in winter. According to the results of backward trajectories and fire spot (Figs. S2 and S3), long-range transmission of biomass burning from north and central China and the local residents' activities were the dominant source of biomass burning on Mt. Wuyi in winter. Extremely high values of levoglucosan appeared on January 1–4 (621.82 ng $m^{-3}$) and February 5–8 (441.87 ng $m^{-3}$), reflecting two biomass burning events. To clarify the characteristics of biomass burning, we checked the Fire Information for Resource Management System (FIRMS, Fig. S2). Obviously, during January 1–4, sporadic fire spots were observed predominantly in Fujian Province where the sampling site is located. However, during February 5–8, active fire spots were located in the northwest and southwest of Fujian Province. Backward trajectories also showed that the air mass came mainly from the southern part of Fujian Province during January 1–4, whereas the air mass originated from the northwest through long-range transport during February 5–8 (Fig. S3). The results indicate

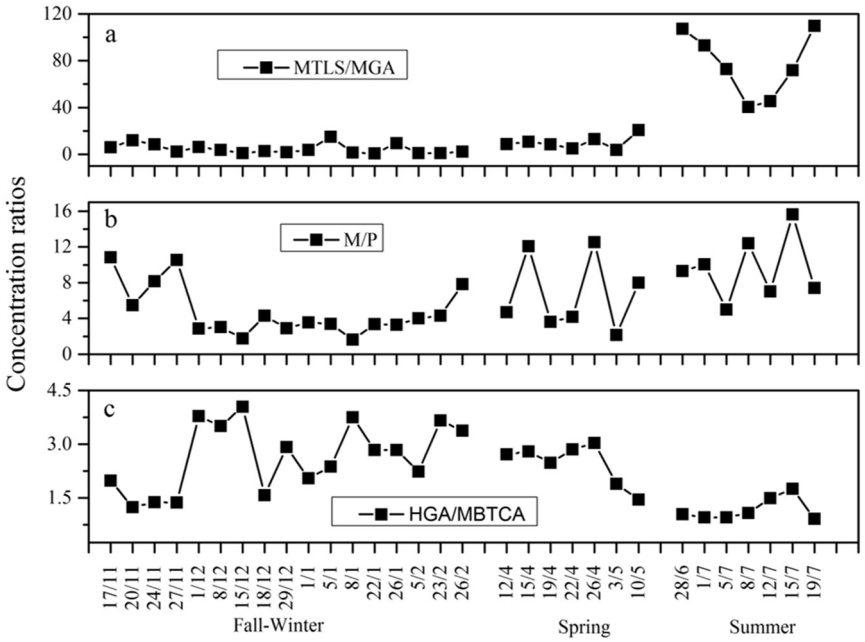



**Fig. 4.** Concentration ratios of (a) MTLs to MGA, (b) M (MBTCA) to P (the sum of PA and PNA), and (c) HGA to MBTCA on Mt. Wuyi during the sampling period. Note: MTLs, MGA, MBTCA, PA, PNA, HGA are the abbreviations of 2-methyltetrols, 2-methylglyceric acid, 3-methyl-1,2,3 butanetricarboxylic acid, pinic acid, pinonic acid, 3-hydroxyglutaric acid, respectively.

that the high levoglucosan concentrations during February 5–8 were caused mainly by regional transport of biomass burning from northwest of the sampling site, whereas local biomass burning was the major source for levoglucosan during January 1–4.

As shown in Fig. 5, the concentrations of DHOPA, malic acid, and β-caryophyllinic acid varied differently for the two biomass burning events. During January 1–4, an obvious peak of levoglucosan was observed, and such peaks were also found for malic acid, DHOPA, and for β-caryophyllinic acid to a lesser extent (Fig. 6). However, during February 5–8, malic acid and DHOPA did not increase along with the increase of levoglucosan concentration, whereas β-caryophyllinic acid exhibited an obvious peak. Malic acid is produced by photochemical reactions of unsaturated hydrocarbons and fatty acids that are emitted from coal combustion and biomass burning (Kawamura and Yasui, 2005; Wang et al., 2010). Previous field studies have demonstrated that biomass/biofuel burning contributes to aromatic hydrocarbons in ambient aerosols in China (Zhang et al., 2013, 2016; Ding et al., 2017). In urban areas, as well as emissions from fossil fuels and solvent use, biomass burning is also an important source of aromatic hydrocarbons (Lewis et al., 2013). In the present study, the temporal trend of malic acid was similar to that of DHOPA (Fig. 6). There was also a significant positive correlation between DHOPA and malic acid ($R^2 = 0.74$, $p < 0.001$) (Fig. S1), suggesting that they have similar emission sources. All the results suggested that malic acid and DHOPA were emitted mainly from biomass burning during the event of January 1–4, whereas they came from biomass burning and other sources (such as fossil fuels combustion and solvent evaporation) during the event of February 5–8. Because of their low volatility, sesquiterpenes (such as β-caryophyllinic acid) can accumulate in wood and leaves and are emitted in large quantities during biomass burning (Ciccioli et al., 2014). In the present study, a positive correlation was found between β-caryophyllinic acid and levoglucosan ($R^2 = 0.6$, $p < 0.01$) (Fig. S1), suggesting that the sources of β-caryophyllinic acid on Mt. Wuyi were regulated by biomass burning.

**Table 3**
Concentrations (ng $m^{-3}$) of α/β-pinene tracers (PA, PNA, HGA, MBTCA, AGA and HDMGA) on Mt. Wuyi during the sampling period.

| Variables | PA | PNA | HGA | MBTCA | AGA | HDMAG |
|---|---|---|---|---|---|---|
| Fall-winter | 0.99 | 0.20 | 9.92 | 4.80 | 0.80 | 4.79 |
| Spring | 1.53 | 0.92 | 19.33 | 8.67 | 1.86 | 11.89 |
| Summer | 1.37 | 0.31 | 14.09 | 12.93 | 2.00 | 4.73 |
| Whole period | 1.22 | 0.41 | 13.32 | 7.80 | 1.37 | 6.55 |

Note: PA, PNA, HGA, MBTCA, AGA and HDMGA are the abbreviations of pinic acid, pinonic acid, 3-hydroxyglutaric acid, 3-methyl-1,2,3 butanetricarboxylic acid, 3-acetylglutaric acid and 3-hydro-4,4-dimethyglutaric acid, respectively.

### 3.4. SOC estimation based on SOA tracers

The SOA tracer method can be used to estimate the SOC from different precursors. The total SOC concentrations on Mt. Wuyi ranged from 0.13 to 1.69 μgC $m^{-3}$, with an average of 0.67 μgC $m^{-3}$. The total isoprene-derived SOC (0.21 ± 0.32 μgC $m^{-3}$) was similar to the β-caryophyllene-derived SOC (0.23 ± 0.32 μgC $m^{-3}$) and was more abundant than the α/β-pinene-derived SOC (0.13 ± 0.10 μgC $m^{-3}$) and toluene-derived SOC (0.08 ± 0.09 μgC $m^{-3}$). The total SOC on Mt. Wuyi was one order of magnitude higher than that in Okinawa (0.036 μgC $m^{-3}$) (Zhu et al., 2016), comparable to that on Mt. Fuji (0.54 μgC $m^{-3}$) (Fu et al., 2014a), and lower than that reported on Mt. Tai (1.65 μgC $m^{-3}$) (Fu et al., 2010). As shown in Fig. 6, the SOC estimated from different precursors varied significantly among the seasons. The isoprene-derived SOC (0.75 ± 0.24 μgC $m^{-3}$) on Mt. Wuyi accounted for roughly 70% of the total SOC in summer. However, the β-caryophyllene-derived SOC (0.48 ± 0.46 μgC $m^{-3}$) in winter (from December 1 to February 26) far exceeded those in the other seasons, accounting for >70% of the total SOC, which were probably attributed to the influence of biomass burning in winter as mentioned previously. Although the DHOPA concentration was low on Mt. Wuyi (approximately 1% of the total SOA concentration; Fig. 2), the estimated toluene SOC (0.08 ± 0.09 μgC $m^{-3}$) accounted for 11.6% of the total SOC (Fig. 6). Because Mt. Wuyi is in the background forest area and there is no anthropogenic pollution within the distance of 50 km, the toluene SOC is produced mainly by the precursors that reached Mt. Wuyi by long-range transport.

## 4. Conclusions

$PM_{2.5}$-bound SOA tracers were investigated at a mountainous site (Mt. Wuyi) in southeastern China. Isoprene SOA tracers originating

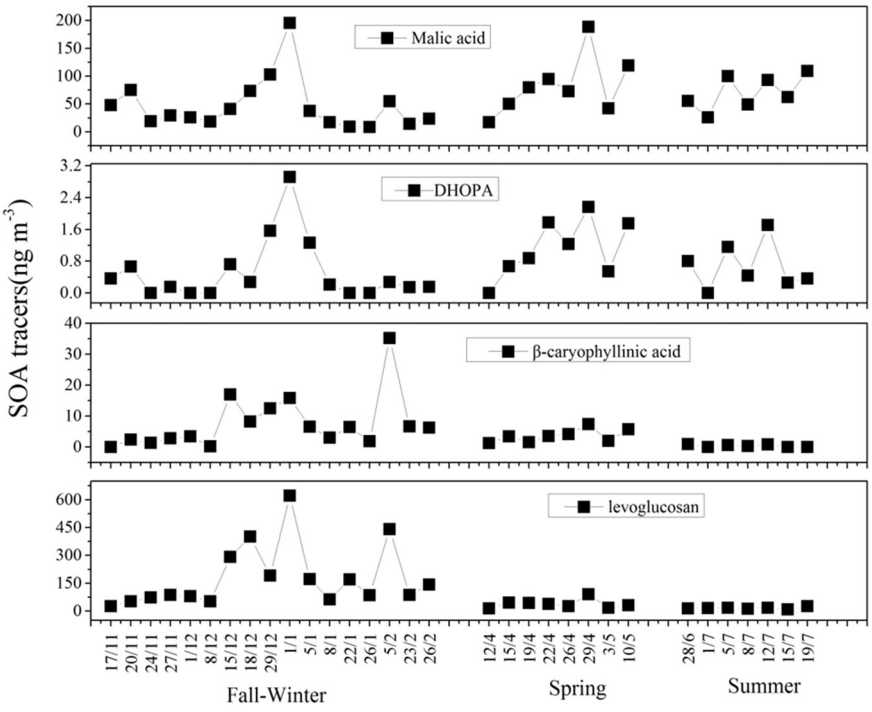



**Fig. 5.** Temporal variations of malic acid, 2,3-Dihydroxy-4-oxopentanoic acid (DHOPA), β-caryophyllinic acid and levoglucosan on Mt. Wuyi during the sampling period.

from biogenic emission showed peak concentrations in summer, indicating the influence of high temperatures and intense light radiation. The α/β-pinene SOA tracers were dominated by MBTCA and HGA, which are the later-generation products of α/β-pinene, indicating that the aerosols are highly oxidized on Mt. Wuyi. Two biomass burning events were identified by the peaks of levoglucosan concentration. SOA tracers such as malic acid and DHOPA increased obviously during the local biomass burning event, while β-caryophyllinic acid peaked during the regional biomass burning event. The tracer-based method was used to estimate the fractions of SOC in $PM_{2.5}$. The isoprene SOC accounted for 70% of the total SOC in summer, whereas the β-caryophyllene SOC was the predominant component in winter. The toluene SOA tracer (i.e. DHOPA) accounted for approximately 1% of the total SOA. However, the estimated toluene SOC contributed 11.6% of the total SOC on Mt. Wuyi. This result suggests that the influence of anthropogenic emissions reached the mountainous forest area by long-range transport cannot be neglected.

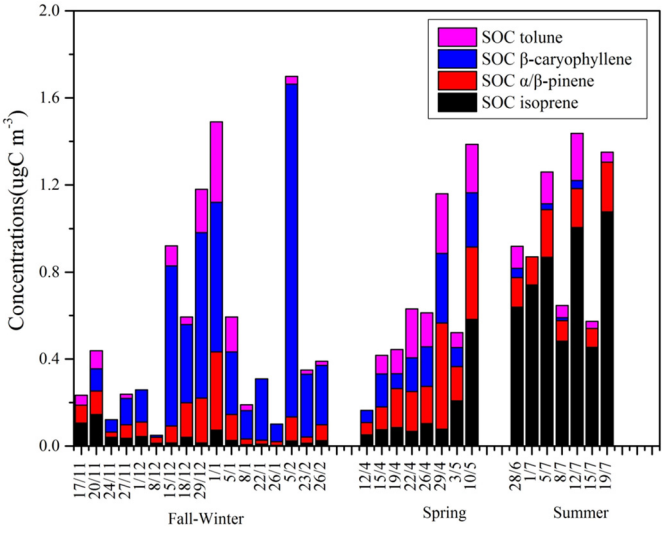



**Fig. 6.** Concentrations of estimated SOC (toluene, β-caryophyllene, α/β-pinene and isoprene) levels on Mt. Wuyi during sampling period.

## Acknowledgement

This research was financially supported by the Chinese Academy of Sciences Interdisciplinary Innovation Team Project, the National Natural Science Foundation of China (NO. U1405235; 41575146; 21507127 & 201607148), the National Key Research & Development Program (NO. 2016YFC02005 & 2016YFE0112200), the Major State Basic Research Development Program of China (NO. 2014CB953802), the Natural Science Foundation of Fujian Province (2016J01201) and STS project in Fujian province (2016T3038).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.370.

## References

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25, 221–241.
Ciccioli, P., Centritto, M., Loreto, F., 2014. Biogenic volatile organic compound emissions from vegetation fires. Plant Cell Environ. 37, 1810–1825.
Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. Science 303, 1173–1176.
D'Ambro, E.L., Lee, B.H., Liu, J., Shilling, J.E., Gaston, C.J., Lopezhilfiker, F.D., Schobesberger, S., Zaveri, R.A., Mohr, C., Lutz, A., 2017. Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low- and high-NOx conditions. Atmos. Chem. Phys. 17, 159–174.
Ding, X., Wang, X., Zheng, M., 2011. The influence of temperature and aerosol acidity on biogenic secondary organic aerosol tracers: observations at a rural site in the central Pearl River Delta region, South China. Atmos. Environ. 45 (6), 1303–1311.
Ding, X., Wang, X., Xie, Z., Zhang, Z., Sun, L., 2013. Impacts of Siberian biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: primary and secondary organic tracers. Environ. Sci. Technol. 47, 3149–3157.
Ding, X., He, Q.F., Shen, R.Q., Yu, Q.Q., Wang, X.M., 2014. Spatial distributions of secondary organic aerosols from isoprene, monoterpenes, β-caryophyllene, and aromatics over China during summer. J. Geophys. Res. 119, 11,877–11,891.

Ding, X., He, Q.F., Shen, R.Q., Yu, Q.Q., Zhang, Y.Q., Xin, J.Y., Wen, T.X., Wang, X.M., 2016. Spatial and seasonal variations of isoprene secondary organic aerosol in China: significant impact of biomass burning during winter. Sci. Rep. 6, 20411.
Ding, X., Zhang, Y.Q., He, Q., Yu, Q.Q., Wang, J.Q., Shen, R.Q., Song, W., Wang, Y., Wang, X., 2017. Significant increase of aromatics-derived secondary organic aerosol during fall to winter in China. Environ. Sci. Technol. 51, 7432–7441.
Duhl, T.R., Helmig, D., Guenther, A., 2008. Sesquiterpene emissions from vegetation: a review. Biogeosciences 5, 761–777.
Eddingsaas, N.C., Loza, C.L., Yee, L.D., Chan, M., Schilling, K.A., Chhabra, P.S., Seinfeld, J.H., Wennberg, P.O., 2012. α-Pinene photooxidation under controlled chemical conditions-part 2: SOA yield and composition in low-and high-NOx environments. Atmos. Chem. Phys. 12, 6489–6504.
Faust, J.A., Wong, J.P., Lee, A.K., Abbatt, J.P., 2017. Role of aerosol liquid water in secondary organic aerosol formation from volatile organic compounds. Environ. Sci. Technol. 51, 1405–1413.
Feng, J., Li, M., Zhang, P., Gong, S., Zhong, M., Wu, M., Zheng, M., Chen, C., Wang, H., Lou, S., 2013. Investigation of the sources and seasonal variations of secondary organic aerosols in $PM_{2.5}$ in Shanghai with organic tracers. Atmos. Environ. 79, 614–622.
Fu, P., Kawamura, K., Chen, J., Barrie, L.A., 2009. Isoprene, monoterpene, and sesquiterpene oxidation products in the high Arctic aerosols during late winter to early summer. Environ. Sci. Technol. 43, 4022–4028.
Fu, P., Kawamura, K., Kanaya, Y., Wang, Z., 2010. Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China. Atmos. Environ. 44, 4817–4826.
Fu, P., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. Biogeosciences 10, 653–667.
Fu, P., Kawamura, K., Chen, J., Miyazaki, Y., 2014a. Secondary production of organic aerosols from biogenic VOCs over Mt. Fuji, Japan. Environ. Sci. Technol. 48, 8491–8497.
Fu, P., Kawamura, K., Cheng, Y.F., Hatakeyama, S., Takami, A., Li, H., Wang, W., 2014b. Aircraft measurements of polar organic tracer compounds in tropospheric particles ($PM_{10}$) over central China. Atmos. Chem. Phys. 14, 328–331.
Fu, P., Aggarwal, S.G., Chen, J., Li, J., Sun, Y., Wang, Z., Chen, H., Liao, H., Ding, A., Umarji, G.S., 2016. Molecular markers of secondary organic aerosol in Mumbai, India. Environ. Sci. Technol. 50, 4659–4667.
Griffin, R.J., Iii, D.R.C., Seinfeld, J.H., Dabdub, D., 1999. Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons. Geophys. Res. Lett. 26, 2721–2724.
Guenther, A., Karl, T., Harley, P., Wiedinmeyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys. 6, 3181–3210.
Haddad, I.E., Marchand, N., Temimeroussel, B., Wortham, H., Piot, C., Besombes, J.L., Baduel, C., Voisin, D., Armengaud, A., Jaffrezo, J.L., 2011. Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille. Atmos. Chem. Phys. 11, 2059–2079.
Hu, D., Bian, Q., Li, T.W.Y., Lau, A.K.H., Yu, J.Z., 2008. Contributions of isoprene, monoterpenes, β-caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. J. Geophys. Res. 113, D22206.
Hu, Q.H., Xie, Z.Q., Wang, X.M., Kang, H., He, Q.F., Zhang, P., 2013. Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic. Sci. Rep. 3, 2280.
Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814–817.
Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Edney, E.O., 2005. Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups. 2. Organic tracer compounds from monoterpenes. Environ. Sci. Technol. 39, 5661–5673.
Jaoui, M., Lewandowski, M., Kleindienst, T.E., Offenberg, J.H., Edney, E.O., 2007. β-Caryophyllinic acid: an atmospheric tracer for β-caryophyllene secondary organic aerosol. Geophys. Res. Lett. 34 (5).
Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S., Zhang, Q., Kroll, J.H., Decarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., 2009. Evolution of organic aerosols in the atmosphere. Science 326, 1525–1529.
Kawamura, K., Yasui, O., 2005. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. Atmos. Environ. 39, 1945–1960.
Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Lewis, C.W., Bhave, P.V., Edney, E.O., 2007. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. Atmos. Environ. 41, 8288–8300.
Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T., Claeys, M., 2008. Polar organic marker compounds in $PM_{2.5}$ aerosol from a mixed forest site in western Germany. Chemosphere 73, 1308–1314.
Lewandowski, M., Jaoui, M., Offenberg, J.H., Kleindienst, T.E., Edney, E.O., Sheesley, R.J., Schauer, J.J., 2008. Primary and secondary contributions to ambient PM in the midwestern United States. Environ. Sci. Technol. 42, 3303–3309.
Lewandowski, M., Piletic, I.R., Kleindienst, T.E., Offenberg, J.H., Beaver, M.R., Jaoui, M., Docherty, K.S., Edney, E.O., 2013. Secondary organic aerosol characterisation at field sites across the United States during the spring–summer period. Int. J. Environ. Anal. Chem. 93, 1084–1103.
Lewis, A.C., Evans, M.J., Hopkins, J.R., Punjabi, S., Read, K.A., Purvis, R.M., Andrews, S.J., Moller, S.J., Carpenter, L.J., Lee, J.D., 2013. The influence of biomass burning on the global distribution of selected non-methane organic compounds. Atmos. Chem. Phys. 13, 851–867.
Li, J.J., Wang, G.H., Cao, J.J., Wang, X.M., Zhang, R.J., 2013. Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects. Atmos. Chem. Phys. 13, 11535–11549.
Lin, Y.H., Knipping, E.M., Edgerton, E.S., Shaw, S.L., 2013. Investigating the influences of $SO_2$ and $NH_3$ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches. Atmos. Chem. Phys. 13, 8457–8470.
Lyu, X.P., Guo, H., Cheng, H.R., Wang, X.M., Ding, X., Lu, H.X., Yao, D.W., Xu, C., 2017. Observation of SOA tracers at a mountainous site in Hong Kong: chemical characteristics, origins and implication on particle growth. Sci. Total Environ. 605–606, 180–189.
Mochida, M., Kawamura, K., Fu, P.Q., Takemura, T., 2010. Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer. Atmos. Environ. 44, 3511–3518.
Offenberg, J.H., Lewis, C.W., Lewandowski, M., Jaoui, M., Kleindienst, T.E., Edney, E.O., 2007. Contributions of toluene and α-pinene to SOA formed in an irradiated toluene/α-pinene/$NO_x$/air mixture: comparison of results using $^{14}C$ content and SOA organic tracer methods. Environ. Sci. Technol. 41, 3972–3976.
Palm, B.B., Campuzanojost, P., Day, D.A., Ortega, A.M., Fry, J.L., Brown, S.S., Zarzana, K.J., Dube, W., Wagner, N.L., Draper, D.C., 2017. Secondary organic aerosol formation from in situ OH, $O_3$, and $NO_3$ oxidation of ambient forest air in an oxidation flow reactor. Atmos. Chem. Phys. 17, 5331–5354.
Paulot, F., Wennberg, P.O., 2009. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. Science 325, 644.
Shen, R.Q., Ding, X., He, Q.F., Cong, Z.Y., Yu, Q.Q., Wang, X.M., 2015. Seasonal variation of secondary organic aerosol tracers in Central Tibetan Plateau. Atmos. Chem. Phys. 15, 8781–8793.
Shrivastava, M., Cappa, C.D., Fan, J., Goldstein, A.H., Guenther, A.B., Jimenez, J.L., Kuang, C., Laskin, A., Martin, S.T., Ng, N.L., Petaja, T., Pierce, J.R., Rasch, P.J., Roldin, P., Seinfeld, J.H., Shilling, J., Smith, J.N., Thornton, J.A., Volkamer, R., Wang, J., Worsnop, D.R., Zaveri, R.A., Zelenyuk, A., Zhang, Q., 2017. Recent advances in understanding secondary organic aerosol: implications for global climate forcing. Rev. Geophys. 55, 509–559.
Simoneit, B.R.T., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129–162.
Stone, E.A., Hedman, C.J., Zhou, J., Mieritz, M., Schauer, J.J., 2010. Insights into the nature of secondary organic aerosol in Mexico City during the MILAGRO experiment 2006. Atmos. Environ. 44, 312–319.
Stone, E.A., Nguyen, T.T., Pradhan, B.B., Dangol, P.M., 2012. Assessment of biogenic secondary organic aerosol in the Himalayas. Environ. Chem. 9, 263–272.
Surratt, J.D., Finlayson-Pitts, B.J., 2010. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. Proc. Natl. Acad. Sci. 107, 6640–6645.
Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. J. Phys. Chem. 110, 9665–9690.
Szmigielski, R., Surratt, J.D., Gómez-González, Y., Veken, P.V.D., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T.E., Lewandowski, M., 2007. 3-Methyl-1,2,3-butanetricarboxylic acid: an atmospheric tracer for terpene secondary organic aerosol. Geophys. Res. Lett. 34, 497–507.
Wang, W., Wu, M.H., Li, L., Zhang, T., 2008. Polar organic tracers in $PM_{2.5}$ aerosols from forests in eastern China. Atmos. Chem. Phys. 8, 12435–12460.
Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., Kawamura, K., 2010. Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation. Atmos. Chem. Phys. 10, 6087–6096.
Zhang, H., Surratt, J.D., Lin, Y.H., Bapat, J., Kamens, R.M., 2011. Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions. Atmos. Chem. Phys. 11, 6411–6424.
Zhang, Y., Wang, X., Barletta, B., Simpson, I.J., Blake, D.R., Fu, X., Zhang, Z., He, Q., Liu, T., Zhao, X., 2013. Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region. J. Hazard. Mater. 250–251, 403–411.
Zhang, Z., Zhang, Y., Wang, X., Lü, S., Huang, Z., Huang, X., Yang, W., Wang, Y., Zhang, Q., 2016. Spatiotemporal patterns and source implications of aromatic hydrocarbons at six rural sites across China's developed coastal regions. J. Geophys. Res. 121, 6669–6687.
Zhu, C., Kawamura, K., Fu, P., 2016. Seasonal variations of biogenic secondary organic aerosol tracers in Cape Hedo, Okinawa. Atmos. Environ. 130, 113–119.